

METHOD OF MAKING STRUCTURED CERAMIC COATINGS AND COATED DEVICES PREPARED WITH THE METHOD

The Field of the Invention

- 5 The present invention relates to a method for low temperature deposition of multi-phase and multi-layered coatings of ceramic compositions with hydraulic binder phases on substrates, which may be metals, polymers as well as ceramics.

10 Background of the Invention

- Some bioceramics are of particular interest within orthopaedics and odontology, e.g. hydroxyapatite, fluoroapatite, calcium phosphates, calcium carbonate and Bioglass®. These materials can also be made more or less bio-resorbable, i.e. they may be dissolved in the body and replaced by natural
15 tissues. This group of ceramics is explored e.g. for orthopaedic metal implants coated with a surface layer of hydroxyapatite, and various bone graft materials based on calcium phosphates and/or calcium carbonates e.g.

- A range of established surface coating techniques have been described. The
20 most established techniques for deposition of ceramic coatings are Chemical Vapour Deposition, Physical Vapour Deposition, Thermal Spraying, Plasma Spraying and Electrolytic Deposition. Surface coatings may also be produced with powder technology.

- 25 A great disadvantage with these techniques for deposition of ceramic coatings, with the exception of electrolytic deposition, is the elevated temperatures involved in their processing. This sets limitations to the selection of substrate materials, and to the chemical structures and phases that can be achieved. To the disadvantage also counts the complexity of the
30 required equipments, such as the gas-tight vacuum arrangements needed for chemical and physical vapour deposition, and the high-temperature and presses required in powder technology.

A recently developed method for the deposition of coatings based on chemically bonded ceramics is described in the patent applications SE-0104440-3, "Coating method and coated devices" (filed December 2001); and
5 SE-0200637-7, "Ceramic surface layers and coated devices (filed March 2002). These patent applications describe a coating deposition method comprising the steps: pre-treatment of substrate; preparation of curable slurry with hydraulic components, deposition of the slurry as a coating on a substrate and hardening of the coating through hydration. Alternatively,
10 layers of non-hydrated hydraulic powders are deposited on the substrate, and hydrated in an additional step.

US-5480438-A, filed September 22, 1993, describes ceramic multi-layers comprising a metallic implant base coated with two bioactive layers. The
15 inner layer can be comprised of calcium aluminate and the outer layer of apatite and/or calcium phosphate. This multi-layer is manufactured by other methods, mainly plasma spraying, than the methods used in the present application. Nor does US-5480438-A disclose multi-layers comprised of hydrated ceramic.

Summary of the Invention

The present invention relates to a method of making structured ceramic coatings and coated devices prepared with the method. More specifically, the present invention relates to a low temperature method for producing multi-
25 layer or multi-phase (multi-structured) coatings and devices covered with such coatings, such as those depicted in Fig. 1. With the technique according to the present invention, surface coatings with controlled variations in terms of chemical composition, phase composition, porosity, surface roughness, mechanical properties, biocompatibility, etc can be
30 achieved.

The present invention provides a method for producing a multi-structured and/or multi-phased ceramic coating in one hydration step. In a basic form, said method comprises application of a non-hydrated ceramic component (or a mixture comprising at least one hydraulic component, which is preferably a phase of calcium aluminate on a substrate, and on top of this layer, a layer of another material, e.g. a biocompatible or bioactive material, and curing said aggregate using a water-based medium. By this method, a multi-structured, a multi-phased ceramic coating, or a combination of the both, can be obtained.

The method according to the present invention can be combined with any coating method involving application of one or more non-hydrated ceramic materials on a substrate. The method according to the present invention is also applicable if the applied ceramic layers are composed of different ceramic materials or comprise mixtures.

The surface coating method according to the present invention is preferably used for producing a biocompatible coating. This biocompatible coating may suitably be used for producing general implants, or specifically implants for orthopaedic and dental applications. The present invention also relates to a device, the surface of which has been coated with a biocompatible coating according to the present invention. The biocompatible coatings may also be used as carriers of therapeutically active drugs, as well as for applications within the fields of micro-structure technology and tribology.

Brief Description of Drawings

Fig. 1. Schematic general drawings of a) homogenous coating, b) multi-phase coating, and c) multi-layered coating, which can be achieved using the coating method according to the present invention.

Fig. 2. Scanning electron cross-section image of double layered coating consisting of a pure hydrated calcium aluminate layer in contact with the substrate and an outer layer of calcium aluminate with 10 wt.% titania.

5 **Detailed Description of the Invention**

The present invention relates to a low temperature method to produce surface coatings based on chemically bonded hydraulic ceramics, in particular all phases of calcium aluminate are applicable to the invention. The present invention describes different ways of controlling the
10 microstructure, porosity, thickness, surface roughness, phase composition and biocompatibility of a coating system.

The method according to the present invention allows the deposition of coating structures combining mechanically strong and chemically stable
15 compounds (primarily hydrated calcium aluminate) with osseocompatible or bio-resorbable compounds, such as hydroxyapatite and calcium carbonate. Coatings may be designed e.g. with an outer layer of the bioresorbable substance, and an inner layer of a hydrated ceramic having better mechanical properties and adhesion to the substrate.

20 One object of the present invention is to provide a surface coating method comprising the steps of preparing several powder mixtures having different chemical composition (in terms of stoichiometry, phases and grain sizes), wherein at least a non-hydrated hydraulic ceramic powder binder phase,
25 pre-treating a substrate surface, to increase the adhesion between the substrate and the ceramic coating, applying said powder mixtures of different chemical composition on the substrate as layers on top of each other, and hydrating the different powder layers in a curing agent. Said non-hydrated hydraulic ceramic powder essentially comprises calcium aluminate,
30 calcium silicate or calcium sulphate or mixtures thereof.

To produce multi-layered structures, the deposition may take place in several consecutive steps. A preferred version involves a first deposited layer containing mainly fine-grained (less 1 μm) calcium aluminate particles, since this produces a dense and mechanically strong layer in contact with the substrate. This is followed by additional depositions of more coarsely grained, or agglomerated dispersions producing rougher and pore porous layers after hydration. An outer layer is then deposited containing larger amounts of bioactive additives such as Bioglass[®], hydroxyapatite or fluoroapatite.

The present invention provides an improved coating method for coating various devices, such as medical devices, which improved coating method is related to the methods described in the earlier patent applications SE-0104440-3, "Coating method and coated devices" (filed December 2001); and SE-0200637-7, "Ceramic surface layers and coated devices (filed March 2002).

Due to the simple application technique for the powders and the low temperatures required for hydration, the chemical composition and the phases of compounds contained in such a composition, as well as the microstructure and porosity of the different layers, can be controlled much better than with the prior art techniques.

Throughout this application the term "biocompatibility" is used a number of times implying certain properties on the material or surface in question. However, it should be noted that biocompatibility is used as a generic term for the different properties that are required or desirable for materials that are to be in contact with biological tissues. Moreover, the materials have also to be used/prepared in the right way and for suitable applications. Another frequently used term is "osseo-compatible", which implies that a material is especially advantageous for use in contact with bone tissue. The term "bioactive" means that a material being stimulates the in-growth of an

implant in for example bone tissue. The term Bioglass® which is used several time in the description is a trade name for a family of phosphorous glasses of good biocompatibility.

5 Multi-phase and multi-layered coatings

In addition to homogenous single-phase coatings, improved performance is often achieved with multi-phase and multi-layered coatings systems.

Reasons to use such coating systems may be to improve the adhesion to the substrate, to increase the toughness, hardness or biocompatibility; to reduce
 10 internal stresses in the coatings; or to control volumetric changes during coating manufacturing. The concepts of multi-phase and multi-layered coatings are illustrated by figure 1.

The different phases or individual layers may be composed of one or several
 15 of the following compounds: calcium aluminates, calcium aluminate hydrates, other hydraulic phases, e.g. calcium sulphate and calcium silicate, fluorapatite, hydroxyapatite, other apatites, calcium phosphates, calcium carbonates, carbonates-apatites mixed phases, Bioglass®, inert phases (non-hydrating phases and calcium aluminate).

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The most preferred hydraulic cement used with the method according to the present invention is various forms of calcium aluminate. But the method is applicable also on other hydraulic cements, such as silicates and sulphates.

25 Like in methods disclosed in previous patent applications SE-0104440-3, "Coating method and coated devices" (filed December 2001); and SE-0200637-7, "Ceramic surface layers and coated devices (filed March 2002), the method comprises the following steps:

30 -Pre-treatment of substrate.

-Preparation of powder particles and dispersions of these in a liquid.

-Deposition of powders particles on a substrate surface, in single or multiple layers

-Hydration of hydraulic component with water, water based solutions or evaporated water

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However, in the method according to the present invention the step of depositing powders particles the substrate surface differs from the above-mentioned methods in that layers of different chemical composition are applied on top of each other.

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Pre-treatment of the substrate

The substrate pre-treatment follows the same procedures as described in SE-0104440-3, "Coating method and coated devices" (filed December 2001).

15 The pre-treatment step is preferably performed with wet or dry sand blasting generating a surface roughness with R_a -values, in the range of 0.1 to 10.0 μm . Also other techniques resulting in similar random surface structures may be applicable, e.g. etching processes, electrolytic processes or abrasive surface treatments. The aim of the blasting is to achieve the anchoring of the
20 coating on the substrate. Also blasting with particles of hydraulic ceramics, preferably CA, is an alternative; this provides seed points (embedded ceramic powder or particles) for the following hydration of the applied ceramic powder. Optionally, but not necessary, the substrate surface may also be
25 pre-treated with hydration accelerating compounds, such as LiCl or other accelerators known within the field. The purpose of the pretreatment with such an accelerator is to initiate the hydrating process in a controlled way directly on the substrate surface, whereby porosity, cracking etc. is avoided at the coating/substrate interface.

30 The substrate used is according to the present invention Ti or alloys thereof, stainless steel, Co-Cr alloys, another biocompatible metal, polymeric or ceramic material, or any combination thereof.

Preparation of powder mixtures and dispersions of these

Preparation of the powder particles involves creation of a selected composition, phase structure and grain size of the hydraulic cement, which
 5 is preferably calcium aluminate or calcium silicates. In a basic form of the present invention, the ceramic powder comprises only hydraulic grains of calcium aluminate, of which several stoichiometries exist. Powders consisting of C_3A , $C_{12}A_7$, CA , CA_2 and CA_6 , where C stands for CaO and A for Al_2O_3 , are all applicable to the present invention. Such powders are
 10 commercially available products.

Said surface coating method may optionally comprise the step of preparing a powder mixture comprising adding particles or powder of one or more biocompatible or bioactive materials composed of particles or powder of one
 15 or several phases containing phosphates, fluorides or carbonates, calcium carbonate, calcium phosphate, apatite, fluoroapatite, carbonates-apatites, hydroxyapatite and Bioglass®.

In addition to the hydraulic component and the additives controlling the
 20 formation of apatites and carbonates, the powder mixture may also contain additives controlling mechanical properties, expansion, curing time, etc.

A non-hydraulic, i.e. non-hydrating, filler may be added as described in our co-pending Swedish patent application SE-0 104 441-1 with the title
 25 "Ceramic material and process for manufacturing". The non-hydraulic filler may comprise calcium titanate or any other ternary oxide of perovskite structure according to the formula ABO_3 , where O is oxygen and A and B are metals, or any mixture of such ternary oxides. A in the perovskite structure is selected from the group comprising Mg, Ca, Sr or Ba, and that the B in the
 30 perovskite structure is selected from the group comprising Ti, Zr, or Hf. The non-hydraulic filler should be present in an amount of less than 30 vol.%, preferably less than 10 vol.% of the total volume of the ceramic ingredients.

But, all material compositions disclosed in said application also apply as coating materials in the present invention.

Also, the expansion controlling additives described in the patent application
5 PCT/SE99/01803, "Dimension stable binding agent systems", are relevant to the present invention, primarily calcium silicates and fumed silica (very finely grained silica).

The surface coating method according to the present invention may also
10 optionally include removing residual water and/or organic material in the powder material.

According to the present invention the surface roughness and porosity are controlled by the choice of particle size of the powder/particle mix. Thus, the
15 method according to the present invention optionally comprises reducing the powder grain size. Small grain sizes allow for smoother coatings and for even coverage of micro-structured surfaces. When these properties are required, the powder grain size is preferably below 10 μm and more preferably between 0.1 and 3 μm . Larger grains and agglomerated grains also produce
20 more porous coatings.

The applied non-hydrated ceramic layer/layers may also be compacted prior to the final hydration. Such compacting can be achieved by using cold isostatic pressing (CIP), hot isostatic pressing (HIP), or by passing a laser
25 beam across the surface. After the compaction step, the degree of compaction of the powder layer is increased between 30 and 80 % and the porosity reduced to 30-45 vol%.

According to the present invention the surface roughness is also controlled
30 by the choice of dispersion liquid for the particle mix. Dispersion liquids of relevance are water, alcohols, oils, acetone, other hydrocarbons, plasticizers, etc. Properties of the liquid to consider are viscosity, vapour pressure,

dispersion effects as well as wettability to powder particles and to substrate. Water or water-based solvents lead to an immediate start of the hydration. Non-water solvents are combined with post-curing, meaning that the actual curing is performed in a separate step.

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Ethanol produces smoother surfaces than acetone due to better dispersion ability. For water-based liquids, the surfaces structure is controlled by the use of water dissolvable dispersing agents and plasticisers.

- 10 For the creation of multi-layered coatings, powder mixtures of different chemical composition and solvents may be prepared for deposition in several subsequent steps.

- 15 Optionally, a component which accelerates or retards the hardening process may be added to the curing agent or the powder material in order to enhance adhesion to a substrate.

Deposition of powders particles on substrate surface

- 20 The powder-solvent mixture is applied to the substrate as one or several thin layers. Various deposition techniques may be used, e.g. dipping, spraying, etc. All deposition techniques described in our co-pending Swedish patent application SE-0200637-7, "Ceramic surface layers and coated devices (filed March 2002) are of relevance to the present invention.

- 25 The application of the powder material on the substrate surface is performed by a thermal spray technique, PVD or CVD deposition techniques, or applied as a tape prepared by tape casting.

- 30 The thickness of the coating is controlled either by the particle size, the dispersion of the particles and the powder-to-solvent ratio. For thick coatings multiple dipping or spraying can be performed.

After deposition of the particle mix, the solvent is evaporated. The evaporation may be performed by letting the particle mixture stand at room temperature in normal atmosphere, but the evaporation process is accelerated at higher temperatures.

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The deposited surface coating according to the present invention has a thickness in the order of 0.1-500 μm , and preferably less than 50 μm .

Post-hydration

- 10 The most relevant procedure of the present invention to cure the deposited particle layer or layers is by post-hydration in a separate step in a water solution, water vapour or an atmosphere of controlled humidity.

- Also the temperature affects the curing procedure. Most relevant for the invention are temperatures between 0°C and 100°C. Preferably, the curing is performed in the range of 20°C to 70°C.
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Coatings and coated devices

- In one embodiment of the method according to the present invention a biocompatible coating is achieved comprising a binding layer in contact with the substrate comprising mainly calcium aluminate particles of less than 2 μm , a bulk layer comprising mainly calcium aluminate having a grain size between 3 and 30 μm , and an outer layer comprising a bioactive material, preferably calcium phosphate, apatite, calcium carbonate or calcium fluoride.
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The biocompatible coatings may also be used as carriers of therapeutically active drugs.

- 30 The present invention also relates to a surface coated device, comprising a substrate and a surface coating covering at least a section of the substrate surface, wherein the surface coating is the biocompatible surface coating

made by using the surface coating method according to the present invention and the substrate is Ti or alloys thereof, stainless steel, Co-Cr alloys, another biocompatible metal, polymeric or ceramic material, or any combination thereof. The surface coated device may be a medical device, medical device for implantation, artificial orthopedic device, spinal implant, joint implant, attachment element, bone nail, bone screw, or a bone reinforcement plate.

EXAMPLE

The surface of a stainless steel substrate, in the form 50 mm long and 4 mm in diameter rods, were pre-treated by sand blasting with 90 mesh aluminum oxide grit to a surface roughness of R_a between 0.6 and 0.7 μm .

A calcium aluminate powder from Lafarge Aluminates, Ternal White® was selected. This is a calcium aluminate with a ratio of Al_2O_3 and CaO of about 70/30. However, any other similar calcium aluminate powder is also possible to use for the same purpose.

The grain size of the calcium aluminate powder was reduced by ball milling. The milling reduced the size of 90% of the grains to less than 10 μm . The milling was performed with a rotating cylindrical plastic container using 10 mm in diameter silicon nitride spheres as milling medium. The milling liquid was iso-propanol. The total milling time was 72 hrs.

After milling, the milling bodies were removed by sieving and the alcohol was evaporated. Thereafter the milled powder was burnt at 400°C for 4 hours, to remove any residual water and organic contamination.

As the bioactive component, hydroxyapatite from Merck with an average grain size of 5 μm was selected.

For the application of a graded coating, two different slurries were prepared. The first slurry, A, consisted of the milled calcium aluminate powder and ethanol mixed with in ration 1:1 by weight. For a second slurry, B, a powder mixture of the same calcium aluminate powder was first mixed 1:1 by weight with hydroxyapatite. This combined powder was mixed in ratio 1:1 by weight with ethanol.

The first layer was applied by dipping the substrate in slurry A, whereafter the ethanol was evaporated in air. The second layer was applied by spraying slurry B on top of the first dried layer. Finally, the ethanol from slurry B was evaporated in air. The dried powder layers remained as a weakly cohesive multi-layered structure, covering the entire substrate.

Thereafter, the samples were hydrated in an upright position in a closed container with a layer of de-ionised water at the bottom at a temperature of 37 °C, leading to a saturated water vapour environment, for 3 days.

The procedure creates a two-layered structure of about 100 μm in total thickness. The inner coating is about 30-60 μm in thickness and consists predominately of calcium aluminate hydrates together with small amounts of non-hydrated calcium aluminates grains. The thickness of the outer layer is between 40 and 70 μm , and contains largely unaffected hydroxyapatite grains in a matrix of predominately calcium aluminate hydrates with traces of non-hydrated calcium aluminate grains.